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Mechanism of Carbon Dioxide Formation in 3130-Å Irradiated Mixtures of Sulfur Dioxide and Carbon Monoxide

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Abstract: Emission and product quantum yield measurements reported here provide a new insight into the mechanism of carbon dioxide formation in SO_2–CO mixtures irradiated within the first singlet absorption band (2400–3200 Å). The quantum yields of sulfur dioxide triplet-sensitized phosphorescence in biacetyl were determined in SO_2–CO–biacetyl mixtures. The kinetic treatment of the data gives the fraction of the excited sulfur dioxide singlet molecules ($^1SO_2$) which generate the emitting triplet ($^3SO_2$) on undergoing quenching collisions with CO: $^1SO_2 + M \rightarrow (SO_2\text{–}M \text{ or products})$ (1); $^1SO_2 + M \rightarrow {}^3SO_2 + M$ (2); $k_2/(k_1 + k_2) = 0.017 \pm 0.010$, where M = CO. The corresponding rate ratio for $M = N_2$ is 0.033. Other emission experiments with SO_2–N_2–biacetyl mixtures show that there is an additional source of SO_2 triplets in experiments above about 5 Torr of reactants. As a result of these two effects the rate of triplet formation is increased markedly on the addition of N_2 to an SO_2–CO mixture. Quantum yields of CO_2 formation have been determined in 3130-Å irradiated mixtures of SO_2 and CO at different CO and SO_2 reactant pressures and with added C_6H_6 and N_2 gases. The kinetics of the C_6H_6-inhibition experiments are consistent with the involvement of the excited fluorescent singlet and the phosphorescent triplet sulfur dioxide molecules in the CO_2 formation reactions. The results confirm the observations of Cehelnik, Spicer, and Heicklen that some state (or states) of SO_2 in addition to the emitting singlet and triplet states is (are) involved in the 3130-Å irradiated SO_2–CO system at high pressures. The tentative mechanism of excess triplet formation in runs at high pressures which is favored here includes an undefined excited state of SO_2 or one of its isomers. The species is not a reactant leading to CO_2 formation, but it presumably generates $^3SO_2$ at high pressures in a collisionally induced reaction.

Carbon monoxide is oxidized when its mixtures with sulfur dioxide are irradiated within either the first allowed absorption band (2400–3200 Å)[1,2] or the forbidden band (3400–3970 Å)[3] of sulfur dioxide. SO_2 is not photodissociated at wavelengths greater than about 2180 Å, so the oxidation of CO must result from an oxygen atom transfer reaction involving some excited species of SO_2. Jackson and Calvert[3] have shown that this excited species is the $^3B_1$ state of SO_2, designated here as $^3SO_2$, when the SO_2 is excited directly to this state by light absorption within the "forbidden" band. However, the situation is not this simple when SO_2 is excited within the first allowed band. Neither the results of Timmons[1] nor those of Cehelnik, Spicer, and Heicklen[2] appear to be compatible with a CO_2-forming mechanism involving $^3SO_2$–CO interactions alone. Thus Timmons found Φ_{CO_2} to be practically independent of the pressure of added CO in his limited series of observations made in experiments at 3130 Å and at a fixed SO_2 pressure. If $^3SO_2$ were the precursor to CO_2 formation in this system, one expects CO_2 formation to be sensitive to the $[SO_2]/[CO]$ ratio.

In contrast to Timmons' observations, Cehelnik, *et al.*,[2] found that Φ_{CO_2} increased markedly with increase in CO pressure, and it was relatively insensitive to SO_2 pressure. They observed further that nitrogen gas addition to the SO_2–CO mixture caused little inhibition of the CO_2 formation. These results seemed inconsistent with the involvement of the known emitting excited states of SO_2 as the only reactants for CO_2 formation, since both the emitting singlet and triplet states of SO_2 are quenched by SO_2, CO, and N_2 gases with efficiencies that are not greatly different.[4,5] Cehelnik, *et al.*, proposed that CO_2 formation involved the

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(1) R. B. Timmons, *Photochem. Photobiol.*, **12**, 219 (1970).

(2) E. Cehelnik, C. W. Spicer, and J. Heicklen, preliminary results presented at the Ninth Informal Photochemistry Conference, The Ohio State University, Columbus, Ohio, Sept 1970; *J. Amer. Chem. Soc.*, **93**, 5371 (1971).

(3) G. E. Jackson and J. G. Calvert, *ibid.*, **93**, 2593 (1971).

(4) H. D. Mettee, *J. Phys. Chem.*, 73, 1971 (1969).

(5) H. W. Sidebottom, C. C. Badcock, G. E. Jackson, J. G. Calvert, G. W. Reinhardt, and E. K. Damon, *Environ. Sci. Technol.*, **6**, 72 (1972).

Table I. Quantum Yields of the $^3SO_2$-Sensitized Phosphorescence (Φ_{sens}) of Biacetyl in SO_2–Ac_2–CO Mixtures Excited at 2875 Å and 27°; [CO] = 2.83[SO_2]

													Av Φ_{sens}(rel)
(a) [SO_2] = 4.74 × 10^{-5} *M*													
[Ac_2], *M* × 10^7	1.79	1.79	2.24	2.68	3.58	4.47	5.81	7.15	8.05	8.50	8.94	8.94	
Φ_{sens} × 10^3	1.66	1.59	1.93	2.02	2.22	2.73	2.84	3.03	3.19	3.21	3.53	3.50	
Φ_{sens} (rel)[a]	0.680	0.707	0.745	0.740	0.709	0.726	0.736	0.753	0.757	0.747	0.749	0.740	0.732
(b) [SO_2] = 5.57 × 10^{-5} *M*													
[Ac_2], *M* × 10^7	2.10	2.10	2.63	3.15	4.20	5.25	6.83	8.41	9.46	9.98	10.5	10.5	
Φ_{sens} × 10^3	1.79	1.71	2.05	2.15	2.42	2.92	3.20	3.28	3.43	3.44	3.78	3.77	
Φ_{sens} (rel)	0.734	0.760	0.792	0.788	0.773	0.777	0.829	0.816	0.814	0.800	0.803	0.797	0.790
(c) [SO_2] = 6.53 × 10^{-5} *M*													
[Ac_2], *M* × 10^7	2.46	2.46	3.08	3.70	4.93	6.16	8.01	9.86	11.1	11.7	12.3	12.3	
Φ_{sens} × 10^3	2.03	1.82	2.22	2.27	2.61	3.14	3.32	3.48	3.65	3.70	3.95	3.95	
Φ_{sens} (rel)	0.832	0.804	0.857	0.832	0.834	0.835	0.860	0.866	0.867	0.860	0.839	0.835	0.844
(d) [SO_2] = 7.69 × 10^{-5} *M*													
[Ac_2], *M* × 10^7	2.90	2.90	3.63	4.35	5.80	7.25	9.43	11.6	13.1	13.8	14.5	14.5	
Φ_{sens} × 10^3	2.15	1.99	2.38	2.44	2.78	3.37	3.60	3.67	3.88	3.90	4.18	4.23	
Φ_{sens} (rel)	0.881	0.884	0.919	0.894	0.888	0.896	0.933	0.913	0.920	0.907	0.887	0.894	0.902
(e) [SO_2] = 9.04 × 10^{-5} *M*													
[Ac_2], *M* × 10^7	3.41	3.41	4.26	5.12	6.82	8.53	11.1	13.6	15.4	16.2	17.1	17.1	
Φ_{sens} × 10^3	2.31	2.14	2.46	2.57	2.96	3.54	3.71	3.78	3.93	3.98	4.45	4.50	
Φ_{sens} (rel)	0.947	0.951	0.950	0.941	0.946	0.941	0.961	0.940	0.933	0.925	0.945	0.951	0.944
(f) [SO_2] = 10.6 × 10^{-5} *M*													
[Ac_2], *M* × 10^7	4.00	4.00	5.00	6.00	8.00	10.0	13.0	16.0	18.0	19.0	20.0	20.0	
Φ_{sens} × 10^3	2.44	2.25	2.59	2.73	3.13	3.76	3.86	4.02	4.21	4.30	4.30	4.73	
Φ_{sens} (rel)	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.000

[a] Φ_{sens} (rel) is the ratio of the Φ_{sens} value in a given column to the Φ_{sens} value for the run at [SO_2] = 10.6 × 10^{-5} *M* given in the same column.

participation of new nonemitting excited singlet and triplet states of SO_2 in addition to the two emitting states. However, the weight of the most compelling evidence for their mechanism, the small effect of added nitrogen gas on Φ_{CO_2}, depends on the correctness of their assumption of the near equal $^3SO_2$ generation rates in the CO–SO_2 and CO–N_2–SO_2 systems. However, this assumption must be questioned in view of other recent observations on these systems.

The kinetics of phosphorescence and fluorescence emission from SO_2 excited within the 2400–3200-Å region at relatively low pressures[4,6–8] show that the $^3B_1$ state of SO_2 is populated largely by a collisional perturbation of the originally excited singlet species ($^1SO_2$).

$$SO_2 + h\nu\ (2400\text{–}3200\ \text{Å}) \longrightarrow {}^1SO_2 \qquad \text{(I)}$$

$$^1SO_2 + M \longrightarrow (SO_2\text{–}M) \qquad (1)$$

$$\longrightarrow {}^3SO_2 + M \qquad (2)$$

(SO_2–M) designates either ground state SO_2 and M molecules or other nonemitting product molecules. Horowitz and Calvert[9] have found recently that the fraction of deactivating collisions which result in $^3SO_2$ formation, $k_2/(k_1 + k_2)$, is dependent on the nature of the collision partner M; for SO_2 excitation at 2875 Å with M = SO_2, N_2, and c-C_6H_{12}, $k_2/(k_1 + k_2)$ = 0.095 ± 0.005, 0.033 ± 0.008, and 0.073 ± 0.024, respectively. Note that if $k_2/(k_1 + k_2)$ is much lower for CO than with N_2 as M, deactivation of $^3SO_2$ by added nitrogen may be masked somewhat by the greater rate of generation of $^3SO_2$ in reaction 2. Obviously some knowledge of this rate ratio for M = CO must be gained before a realistic evaluation can be made of the possible role of the $^3SO_2$ state in this system.

In this work we have photolyzed SO_2–CO mixtures and have determined the $k_2/(k_1 + k_2)$ ratio for M = CO. We have also redetermined the effect of CO and SO_2 reactant pressures and added N_2, C_6H_6, and biacetyl vapors on the quantum yields of CO_2. These data are compared with the findings of previous workers, and the possible mechanisms of CO_2 formation are considered for the SO_2–CO mixtures excited within the first absorption band.

Experimental Methods and Results

SO_2-Sensitized Biacetyl Phosphorescence Studies. The emission studies performed in this work utilized an absolute spectrofluorometer (Turner, Model 210). Previous studies have shown that the intersystem crossing ratios, $k_2/(k_1 + k_2)$, and the relative fluorescence quenching rate constants for SO_2 mixtures are relatively insensitive to the SO_2 excitation wavelength. Thus we have chosen for our emission studies wavelength 2875 Å, the region of maximum absorption by SO_2, to maximize the phosphorescence and fluorescence signal intensities and the accuracy of the determinations. The rate data should apply well in the treatment of the 3130-Å product quantum yield data. The techniques employed were the same as those described previously.[9] The quantum yields of the $^3SO_2$-sensitized phosphorescence of biacetyl (Φ_{sens}) in SO_2–CO–biacetyl mixtures are summarized in Table I for several different reactant concentrations. Data from similar experiments from SO_2–biacetyl mixtures with added high concentrations of nitrogen gas are shown in Table II. Data from the SO_2 fluorescence quenching experiments with added CO_2, required in the kinetic evaluation of the intersystem crossing ratio of $^1SO_2$ perturbed by CO collisions, are given in Table III.

CO_2 Product Quantum Yield Studies from SO_2–CO Mixture Photolyses. Dr. George Jackson devised much of the apparatus and techniques employed for the purification of CO and for the

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(6) H. D. Mettee, *J. Chem. Phys.*, **49**, 1784 (1968).

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(8) (a) T. N. Rao, S. S. Collier, and J. G. Calvert, *J. Amer. Chem. Soc.*, **91**, 1609 (1969); (b) *ibid.*, **91**, 1616 (1969); (c) T. N. Rao and J. G. Calvert, *J. Phys. Chem.*, 74, 681 (1970).

(9) A. Horowitz and J. G. Calvert, *Int. J. Chem. Kinet.*, 4, 175, 191 (1972).

Table II. Effect of Nitrogen on the $^3SO_2$-Sensitized Phosphorescence of Biacetyl Excited at 2875 Å and 28°; $[SO_2] = 7.93 \times 10^{-4}\ M$; $[Ac_2] = 3.17 \times 10^{-6}\ M$

$[N_2]$, $M \times 10^3$	$\Phi_{sens}/\Phi^0_{sens}$[a]	θ[b]	κ[c]	$(\Phi_{sens}/\Phi^0_{sens})\theta\kappa$
0.85	0.877	1.332	1.095	1.28
1.90	0.780	1.743	1.213	1.65
2.20	0.731	1.860	1.246	1.69
2.85	0.740	2.114	1.319	2.06
3.87	0.626	2.513	1.433	2.25
6.06	0.631	3.369	1.679	3.57
10.5	0.581	5.106	2.176	6.46
15.7	0.563	7.139	2.758	11.1
20.7	0.547	8.090	3.318	14.7
24.0	0.534	10.30	3.688	20.3
24.2	0.510	10.46	3.710	19.8
25.0	0.520	10.77	3.800	21.3
29.0	0.521	12.34	4.248	27.3
32.3	0.465	13.63	4.618	29.3
35.3	0.433	14.80	4.953	31.8

[a] Φ^0_{sens} and Φ_{sens} are the biacetyl sensitized phosphorescence quantum yields in the absence and presence of nitrogen, respectively. [b] $\theta = 1 + \{(k_{1d} + k_{2d})[N_2]/(k_{1a} + k_{2a})[SO_2]\}$ [c] $\kappa = 1 + \{k_{9c}[N_2]/(k_{10}[Ac_2] + k_8[SO_2])\}$.

Table III. Effect of Carbon Monoxide on the Quantum Yield of $^1SO_2$ Fluorescence at 27°; Excitation Wavelength, 2875 Å; $[SO_2] = 5.0 \times 10^{-5}\ M$[a]

$[CO]/[SO_2]$	ϕ_f^0/ϕ_f	$[CO]/[SO_2]$	ϕ_f^0/ϕ_f
0.60	1.21	3.00	2.06
1.00	1.35	4.00	2.40
2.00	1.69	5.00	2.76

[a] The ϕ_f^0 and ϕ_f indicate the quantum yields of fluorescence of $^1SO_2$ in pure SO_2 at $5.0 \times 10^{-5}\ M$ and that for the SO_2–CO mixtures at the same $[SO_2]$ and at the concentration ratio shown, respectively.

Table IV. Quantum Yields of Carbon Dioxide from the Photolysis of SO_2–CO Mixtures at 30° and 3130 Å

Pressure, Torr		Quantum yield of $CO_2 \times 10^3$	
SO_2	CO	Exptl	Calcd[a]
2.00	25	3.3	4.2
2.00	111	6.1	6.8
2.00	196	9.2	9.6
2.00	283	12.3	12.4
2.00	376	18.0	15.4
2.21	375	15.8	15.3
2.87	100	5.5	6.5
4.43	44.8	3.4[b]	4.7
4.64	5.93	0.90	2.0
4.64	8.70	1.2	2.5
4.64	11.2	1.4	2.8
4.64	25.4	2.3	3.9
4.64	111	6.2	6.8
4.64	129	7.0[c]	7.3
4.64	131	6.9	7.4
4.64	167.4	7.5	8.5
4.64	209	8.6	9.9
4.64	234	10.4	10.6
4.64	341	14.4	14.0
4.64	376	13.5	15.2
4.64	428	14.8	16.8
6.58	230	9.7	9.8
8.00	280	12.2	11.1
11.0	25	1.8	2.0
11.0	111	6.0	5.4
11.0	155	6.9	6.8
11.0	196	8.5	8.0
11.0	284	10.8	10.7
11.0	375	13.8	13.5
15.0	150	7.5	6.1
22.0	220	10.0	7.3
22.0	220	8.7[c]	7.3
22.0	375	16.0	13.9
30.0	25	1.6	1.6
30.0	111	5.4	3.5
30.0	111	5.0[c]	3.5
30.0	111	5.2[c]	3.5
30.0	196	8.5	5.9
30.0	284	10.9	8.3
30.0	375	14.9	10.8
44.0	375	15.0	9.5

[a] Calculated using equations F, G, and N of the text. [b] Average of four experiments at these conditions. [c] Runs made using samples of highly purified Airco CO; in all other runs the CO was purified by the distillation technique described in the text.

recovery of CO_2 following the photolyses.[3] The quartz reaction vessel for the photolyses at 3130 Å was a cylindrical cell having a diameter of 3.5 cm and a length of 40 cm. The cell was in series with a magnetically operated circulating pump which ensured proper mixing of the reactant gases. Light from a high-pressure mercury arc (PEK 500-3) was filtered through the following solutions: $NiSO_4$ (0.178 M, 5 cm), K_2CrO_4 ($5.0 \times 10^{-4}\ M$, 5 cm), potassium biphthalate (0.0245 M, 1 cm) and a Corning glass filter, 7-54 (9863), 0.3 cm. Radiation exiting from the reaction cell was attenuated with a uniform density filter and monitored with a RCA-935 phototube.

Several experiments were performed using 3530–3970-Å radiation; the filter system employed and the methods of estimation of Φ_{CO_2} have been described previously.[3] In these photolyses we employed a cylindrical Pyrex cell having a diameter of 5.5 cm and a length of 48 cm.

A grease-free vacuum line was used in all experiments. Pressure readings were made with a quartz spiral manometer.

The reactant gases CO and SO_2 were purified as described previously.[3] Spectroquality benzene (Matheson Coleman and Bell) was degassed and vacuum distilled, and a middle third was retained for use. Nitrogen (Air Products) with a stated purity greater than 99.99% was used without further purification. It has been reported that $Fe(CO)_5$ present in CO obtained from steel cylinders may promote the oxidation of NO to NO_2.[10] The CO from our purification train showed no detectable $Fe(CO)_5$ in mass spectrometric analyses (less than 0.25%). However, a test was made for the possible influence of undetectable traces of $Fe(CO)_5$ in the CO through the use of highly purified CO from Airco Industrial Gases; the only impurities noted were N_2, 400 ppm, and CO_2, 4 ppm. The results obtained using this CO were indistinguishable, within the experimental error, from runs under similar conditions using the CO purification techniques of Jackson and Calvert.[3] After each photolysis the reaction mixture was pumped slowly through two glass helix-packed tubes in conjunction with the gas chromatographic injector loop maintained at −196°. When all but a few Torr of the CO had been pumped away, the injector loop was allowed to warm to room temperature, and the sample was injected into the gas chromatograph (modified Aerograph Model A-700 with a 12 ft Porapak Q column maintained at 35 °C).

The incident light intensity was measured at regular intervals using potassium ferrioxalate actinometry. The fraction of the incident light absorbed was measured in each experiment with the phototube. The phototube response was calibrated as a function of the incident light intensity with the photolysis cell evacuated. Within the range of SO_2 pressures, 2–11 Torr, the absorption followed well the Beer–Lambert law with $\epsilon = [\log (I_0/I)]/cl = 29.7$ l./(mol cm).

The quantum yields of CO_2 formation for SO_2–CO mixtures at 3130 Å are summarized in Table IV. Those for SO_2–CO mixtures with added gases, C_6H_6 and N_2, are given in Table V.

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(10) K. Westberg, N. Cohen, and K. W. Wilson, *Science*, 171, 1013 (1971).

Table V. Quantum Yields of Carbon Dioxide from the Photolysis of SO_2–CO Mixtures with Added C_6H_6 and N_2 Gases at 30°

Pressure, Torr				
SO_2	CO	C_6H_6	N_2	$\Phi_{CO_2} \times 10^3$
(a) Wavelength, 3130 Å				
2.21	375	7.00	0.0	2.45
4.64	111	0.0404	0.0	5.42
4.64	111	0.0983	0.0	4.36
4.64	111	0.130	0.0	4.14
4.64	111	0.173	0.0	3.89
4.64	111	0.286	0.0	3.23
4.64	111	0.830	0.0	2.22
4.64	111	1.46	0.0	2.05
4.64	111	2.00	0.0	1.72
4.64	111	2.42	0.0	1.49
4.64	111	2.42	0.0	1.76
4.64	111	2.42	0.0	1.88
4.64	111	2.58	0.0	1.50
4.64	111	2.58	20	1.56
4.64	111	2.58	48	1.18
4.64	111	2.58	74	1.31
4.64	111	2.58	148	1.19
4.64	111	2.58	153	1.24
4.64	111	2.58	169	1.29
4.64	111	2.58	216	1.11
4.64	111	2.58	291	1.37
4.64	111	3.04	0.0	1.43
4.64	375	7.00	0.0	2.15
11.0	375	3.00	0.0	3.14
11.0	375	5.00	0.0	2.15
11.0	375	7.00	0.0	1.95
22.0	375	7.00	0.0	2.33
44.0	375	7.00	0.0	2.22
(b) Wavelengths, 3530–3970 Å				
94.0	213	0.0	0.0	26.4
94.0	213	0.0	0.0	27.8
94.0	213	0.0	300	21.1
94.0	213	0.0	300	17.0

Discussion of the Results

The kinetics of the product formation in the 2400–3200-Å photolyses of pure sulfur dioxide,[11] SO_2–paraffin hydrocarbon mixtures,[12] and SO_2–olefin mixtures[13] seem consistent with the involvement of the first excited triplet state ($^3B_1$) of sulfur dioxide, designated here as $^3SO_2$. When $^3SO_2$ species in SO_2–CO mixtures were generated directly by adsorption within the "forbidden" $SO_2(^1A_1) \rightarrow SO_2(^3B_1)$ band, the rates of CO_2 formation were also explicable in terms of the $^3SO_2$ and CO reactants.[3] On the other hand, Cehelnik, *et al.*,[2] have found that a simple mechanism involving $^3SO_2$ as the only reactant to form CO_2 was entirely inadequate to explain the 3130-Å photolysis of SO_2–CO mixtures. They invoked the participation of not only the emitting singlet and triplet states but also two new nonemitting triplet and singlet states. However, no firm conclusions can be made regarding the extent of involvement of the optical states until reasonable estimates have been determined for the relative rates of reactions 1 and 2 with CO as M. Such an estimate is possible from our data reported in Table I.

Intersystem Crossing Ratio Induced in $^1SO_2$ on Collision with CO Molecules. Estimates of the rate of $^3SO_2$ generation in SO_2–CO mixtures can be had from a study of the $^3SO_2$-sensitized emission in biacetyl. Consider the following mechanism for the reactions of the fluorescent ($^1SO_2$) and phosphorescent ($^3SO_2$) states in the SO_2–CO–biacetyl containing mixtures;[14] the first-order decay reactions of both the singlet and triplet states can be neglected for the reactant pressures employed here.

$$SO_2 + h\nu\ (2400\text{–}3200\ \text{Å}) \longrightarrow {}^1SO_2 \qquad \text{(I)}$$

$$^1SO_2 + SO_2 \longrightarrow (2SO_2 \text{ or products}) \qquad \text{(1a)}$$

$$\longrightarrow {}^3SO_2 + SO_2 \qquad \text{(2a)}$$

$$^1SO_2 + CO \longrightarrow (SO_2, CO, \text{ or products not } CO_2) \qquad \text{(1b)}$$

$$^1SO_2 + CO \longrightarrow SO + CO_2 \qquad \text{(1c)}$$

$$\longrightarrow {}^3SO_2 + CO \qquad \text{(2b)}$$

$$^3SO_2 + SO_2 \longrightarrow SO_3 + SO \qquad \text{(8a)}$$

$$\longrightarrow (2SO_2 \text{ or products not } SO_3) \qquad \text{(8b)}$$

$$^3SO_2 + CO \longrightarrow SO + CO_2 \qquad \text{(9a)}$$

$$\longrightarrow (SO_2, CO, \text{ or products not } CO_2) \qquad \text{(9b)}$$

$$^3SO_2 + Ac_2 \longrightarrow SO_2 + {}^3Ac_2 \qquad \text{(10)}$$

$$^3Ac_2 \longrightarrow Ac_2 + h\nu_p' \qquad \text{(11)}$$

$$\longrightarrow Ac_2 \qquad \text{(12)}$$

$$^3Ac_2 + \text{Wall} \longrightarrow Ac_2 + \text{Wall} \qquad \text{(13)}$$

$^3Ac_2$ represents the phosphorescent triplet state of biacetyl. The measured quantum yields of sensitized emission from the biacetyl triplets are summarized in Table I. The methods of treating the data are identical with those reported recently by Horowitz and Calvert[9] for the SO_2–biacetyl, SO_2–N_2–biacetyl, and SO_2–cyclohexane–biacetyl systems, and they need not be considered in detail here. In all of the runs in Table I, the reactant ratio, $[CO]/[SO_2]$, was fixed at 2.83. For these conditions the mechanism outlined predicts that the reciprocal of the quantum yield of biacetyl triplet formation (Φ_T) will be given by relation A. As described previously,[9] the function α, the fraction of the total biacetyl triplets formed which decay homogeneously in reactions 11 and 12, can be derived from the plot of the average values of $1/\phi_{sens}$ (rel) *vs.* the reciprocal of the total concentration of the reactants. See Figure 1. The slope and intercept of this plot give upon normalization the following relation for α.[9]

$$\frac{1}{\Phi_T} = \left(\frac{\alpha}{\Phi_{sens}}\right)\left(\frac{k_{11}}{k_{11} + k_{12}}\right) = \frac{\beta}{[Ac_2]} + \gamma \qquad \text{(A)}$$

$$\frac{1}{\alpha} = 1 + \frac{(1.21 \pm 0.04) \times 10^{-4}\ M}{[SO_2] + [CO]} \qquad \text{(B)}$$

The parameters β and γ in relation A are complex functions of the $[SO_2]/[CO]$ ratio and various rate constants; they are constants for any series of runs at a fixed $[SO_2]/[CO]$ ratio.[9] We may assign the rate constant ratio $k_{11}/(k_{11} + k_{12}) = 0.15$ in relation A.[9] Now the mechanism I-13 demands that a plot of the function

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[11] S. Okuda, T. N. Rao, D. H. Slater, and J. G. Calvert, *J. Phys. Chem.*, 73, 4412 (1969).

[12] C. C. Badcock, H. W. Sidebottom, J. G. Calvert, G. W. Reinhardt, and E. K. Damon, *J. Amer. Chem. Soc.*, **93**, 3115 (1971).

[13] H. W. Sidebottom, C. C. Badcock, J. G. Calvert, B. R. Rabe, and E. K. Damon, *ibid.*, **93**, 3121 (1971).

[14] The numbering of the reactions follows that used in the previous studies.

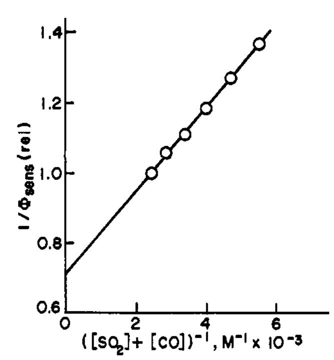

Figure 1. Plot of the reciprocal of the relative quantum yield of $^3SO_2$-sensitized emission in biacetyl *vs.* the reciprocal of the total pressure of CO and SO_2; data are from the 2875-Å irradiated SO_2–CO–biacetyl mixtures of Table I; $[CO]/[SO_2] = 2.83$; temperature, 27°.

$\alpha(0.15)/\phi_{sens}$ *vs.* $1/[Ac_2]$ at a series of fixed SO_2 concentrations should give a series of straight lines with a common intercept γ and with slopes β which are proportional to the $[SO_2]$. These plots are shown in Figure 2 and the parameters which determine the least-squares lines are summarized in Table VI. It can be seen that the intercepts of the various lines are equal within the experimental error as demanded by the mechanism.

Table VI. Summary of the Parameters for the Least-Squares Lines of Figure 2

$[SO_2]$, 10^5 *M*	Slope (β), 10^6 *M*	Intercept (γ)	Slope/intercept, 10^7 *M*
4.74	5.49 ± 0.44[a]	17.3 ± 1.4	3.18 ± 0.51
5.57	6.52 ± 0.46	17.1 ± 1.3	3.81 ± 0.56
6.53	7.23 ± 0.76	17.8 ± 1.8	4.05 ± 0.83
7.69	8.31 ± 0.78	18.0 ± 1.5	4.61 ± 0.81
9.04	9.39 ± 1.03	18.8 ± 1.7	5.00 ± 1.00
10.6	11.1 ± 1.2	18.5 ± 1.7	6.00 ± 1.20
	Av intercept	17.8 ± 0.6	

[a] The error values shown throughout this work are the 95% confidence limits (2σ values) calculated assuming that only random errors exist in the measurements.

A further check on the consistency of the data is had from the $[SO_2]$ dependence of the slope/intercept ratios of the family of curves of Figure 2. In theory one expects relation C to apply. From our experiments

$$\left(\frac{\text{slope}}{\text{intercept}}\right)_{\text{Figure 2}} = [SO_2]\left(\frac{k_{8a}+k_{8b}}{k_{10}} + \frac{[CO](k_{9a}+k_{9b})}{[SO_2]k_{10}}\right) \quad \text{(C)}$$

at constant $[CO]/[SO_2]$ ratio, the slope/intercept ratio should be proportional to $[SO_2]$. This is seen to be the case in the plot of these data in Figure 3. The error in the intercept is too great to allow a meaningful test of its significance, but the least-squares slope of this line, $(4.48 \pm 0.61) \times 10^{-3}$, the reactant ratio $[CO]/[SO_2] = 2.83$, and previous estimates from $^3SO_2$ lifetime data, $k_{8a} + k_{8b} = (3.9 \pm 0.1) \times 10^8$,[15] $k_{10} = (1.4 \pm 0.1) \times 10^{11}$ l./(mol sec),[13] when substituted into relation C give the estimate, $k_{9a} + k_{9b} = (8.4 \pm 3.2) \times 10^7$ l./(mol sec). This checks well with Jackson and Calvert's previous direct determination from $^3SO_2$ lifetime measurements, $k_{9a} + k_{9b} = (8.4 \pm 0.6) \times 10^7$ l./(mol sec),[3] and adds support as to the correctness of the mechanism choice.

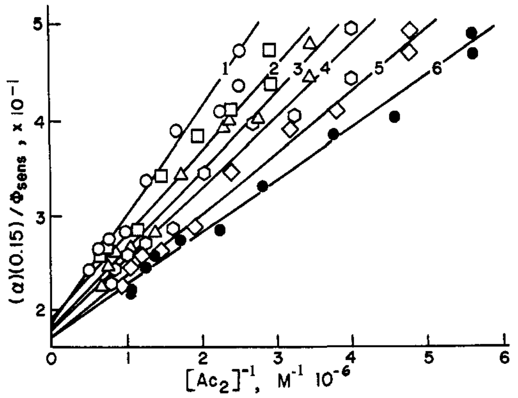

Figure 2. Plot of the function of Φ_{sens}, equal in theory to the reciprocal of the quantum yield of formation of triplet biacetyl molecules (relation A of the text[9]) *vs.* the reciprocal of the biacetyl concentration; the data are from the 2875-Å photolyses of SO_2–CO–biacetyl mixtures at 27° and the following sulfur dioxide concentrations ($M \times 10^5$): curve 1 (circles), 10.6; 2 (squares), 9.04; 3 (triangles), 7.69; 4 (hexagons), 6.53; 5 (diamonds), 5.57; 6 (closed circles), 4.74.

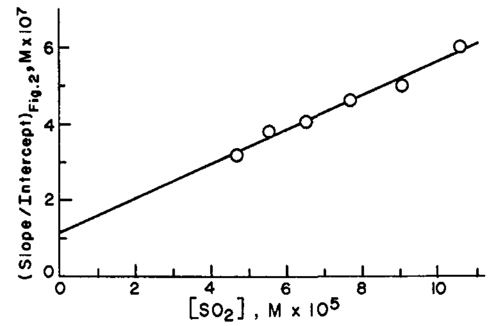

Figure 3. Plot of the slope/intercept ratios, derived from the data of Figure 2, *vs.* the sulfur dioxide concentration; data are from the 27°, 2875-Å photolyses of CO–SO_2–biacetyl mixtures.

In terms of the reaction mechanism the rate constant ratio k_{2b}/k_{2a} is related to the intercept γ of the plots in Figure 2 by relation D. In order to evaluate k_{2b}/k_{2a}

$$\frac{k_{2b}}{k_{2a}} = \left\{\frac{k_{1a}+k_{2a}}{k_{2a}\gamma}\left[1 + \left(\frac{k_{1b}+k_{1c}+k_{2b}}{k_{1a}+k_{2a}}\right) \times \frac{[CO]}{[SO_2]}\right] - 1\right\}\frac{[SO_2]}{[CO]} \quad \text{(D)}$$

one additional rate constant ratio is required: the relative quenching rate constants for excited singlet SO_2 quenching by CO and SO_2, $(k_{1b} + k_{1a} + k_{2b})/(k_{1a} + k_{2a})$. This can be obtained from the fluorescence quenching data of Table III. The Stern–Volmer plot of these data is given in Figure 4. The form is that expected in terms of the theoretical expression E.

$$\frac{\phi_f^0}{\phi_f} = 1 + \frac{(k_{1b}+k_{1c}+k_{2b})}{(k_{1a}+k_{2a})}\frac{[CO]}{[SO_2]} \quad \text{(E)}$$

ϕ_f^0 and ϕ_f are the quantum yields of SO_2 fluorescence in pure SO_2 and in SO_2–CO mixtures at the same $[SO_2]$. The slope of the line in Figure 4 gives $(k_{1b} + k_{1c} +$

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(15) H. W. Sidebottom, C. C. Badcock, J. G. Calvert, G. W. Reinhardt, B. R. Rabe, and E. K. Damon, *J. Amer. Chem. Soc.*, 93, 2587 (1971).

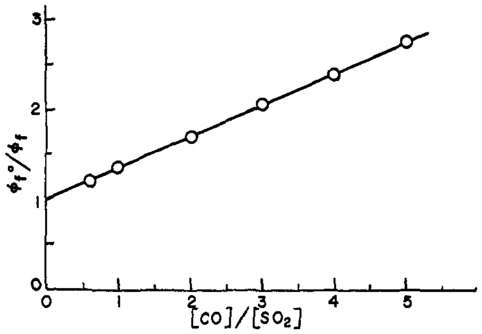

Figure 4. Plot of the ratio of SO_2 fluorescence quantum yields in pure SO_2 to those in SO_2–CO mixtures at the same $[SO_2]$ *vs.* the ratio $[CO]/[SO_2]$; data are from experiments at 2875 Å and 27°.

$k_{2b})/(k_{1a} + k_{2a}) = 0.35 \pm 0.01$, identical with the value observed previously by Mettee.[4] Substituting this into relation D together with $k_{2a}/(k_{1a} + k_{2a}) = 0.095 \pm 0.005$,[9] $[CO]/[SO_2] = 2.83$, and our average intercept of Figure 2, $\gamma = 17.8 \pm 0.6$, we find $k_{2b}/k_{2a} = 0.063 \pm 0.027$, and $k_{2b}/(k_{1b} + k_{1c} + k_{2b}) = 0.017 \pm 0.007$.[16] Recall that the analogous intersystem crossing ratio for M = N_2 was 0.033. Thus CO appears to be considerably less efficient than nitrogen in inducing intersystem crossing in $^1SO_2$.

Evaluation of the Role of $^3SO_2$ in CO_2 Formation as Estimated from the Rate Constants Derived from Mixtures of CO and SO_2 at Low Pressures. If the low-pressure reaction sequence holds as well for the high-pressure systems employed in the runs of Table IV, then the quantum yield of carbon dioxide $\Phi_{CO_2}{}^T$ which can be derived from the $^3SO_2$ reactant should be given by relation F. We have now determined all of the rate

$$\Phi_{CO_2}{}^T = \frac{\left(\dfrac{k_{9a}}{k_{9a} + k_{9b}}\right)\left(\dfrac{k_{2a}}{k_{1a} + k_{2a}}\right)\left(\dfrac{[SO_2]}{[CO]} + \dfrac{k_{2b}}{k_{2a}}\right)}{\left(\dfrac{[SO_2]}{[CO]} + \dfrac{k_{1b} + k_{2b} + k_{1c}}{k_{1a} + k_{2a}}\right)\left(\dfrac{[SO_2](k_{8a} + k_{8b})}{[CO](k_{9a} + k_{9b})} + 1\right)} \qquad \text{(F)}$$

constant ratios that appear in relation F, and we may evaluate Φ_{CO_2} for any $[CO]/[SO_2]$ ratio using the present estimates for $k_{2b}/k_{2a} = 0.063$ and $(k_{1b} + k_{2b} + k_{1c})/(k_{1a} + k_{2a}) = 0.35$, together with the previous estimates; $k_{9a}/(k_{9a} + k_{9b}) = 0.085$[3], $k_{2a}/(k_{1a} + k_{2a}) = 0.095$,[9] $(k_{8a} + k_{8b})/(k_{9a} + k_{9b}) = 4.7$.[3,15,17] It can be shown readily from these data and relation F that the maximum value of $\Phi_{CO_2}{}^T = 2.02 \times 10^{-3}$ is reached at $[SO_2]/[CO] = 0.144$. An inspection of the results of Table IV shows that the experimentally measured Φ_{CO_2} rises to values almost ten times this theoretical maximum at high CO pressures. If the mechanism of $^3SO_2$ generation which is operative at low pressures is the only source of this state at the high pressures of reactants used in the quantum yield studies, then the $^3SO_2$ species can account for only a small part of the total CO_2 formation, as originally suggested by Cehelnik, *et al.*[2] We will return to a consideration of this point after an examination of our results of the triplet quenching studies.

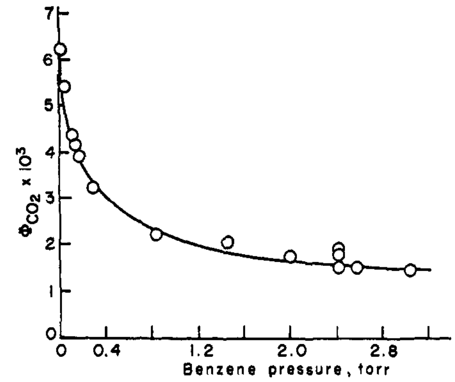

Figure 5. Plot of the quantum yield of carbon dioxide in 3130-Å irradiated mixtures of SO_2 and CO as a function of added benzene pressure; $P_{SO_2} = 4.64$, $P_{CO} = 111$ Torr; temperature, 30°.

An Estimate of the Extent and the Nature of the Singlet Excited SO_2 Involvement in CO_2 Formation in SO_2–CO Mixture Photolyses. The photolyses of the CO–SO_2 mixtures were inhibited by benzene addition in a series of runs at fixed pressures of SO_2 (4.64) and CO (111 Torr). These are summarized in Table V. The rate constant for $^3SO_2$ quenching by benzene is about 1000 times that for CO.[13] Note in Figure 5 the effectiveness of small quantities of benzene in quenching a large part of the CO_2 product formed; for these conditions Φ_{CO_2} is reduced from 6.23×10^{-3} in the absence of benzene to 1.45×10^{-3} for benzene pressures greater than about 3 Torr. The concentration of the excited singlet fluorescent state of SO_2 could not have been altered significantly by the benzene addition,[18] so that the benzene-inhibited quantum yields of CO can be treated simply to extract the contribution from the singlet state or states involved. Some evidence can be gained from our quenching data concerning the nature of the singlet molecule leading to CO_2. Cehelnik, *et al.*, suggested that two different excited singlets, the emitting and a nonemitting singlet state, are involved in this system. It is instructive to test first the simplest possible case, the involvement of the initially excited fluorescent singlet species ($^1SO_2$) alone. Assuming this, the mechanism outlined in I-13 predicts that the contribution of the excited singlet to the quantum yield of CO_2 formation ($\Phi_{CO_2}{}^S$) will be given by relation G.

$$\Phi_{CO_2}{}^S = \frac{(k_{1c}/(k_{1b} + k_{1c} + k_{2b}))}{(1 + ([SO_2]/[CO])2.86)} \qquad \text{(G)}$$

By using the quenching function, relation H, obtained from the benzene inhibition experiments to be considered in detail later, we can correct the measured Φ_{CO_2} values to 100% triplet quenching and estimate $\Phi_{CO_2}{}^S$ for the various runs in Table IV. If the mechanism choice is correct, then in theory the product of $\Phi_{CO_2}{}^S$ and the factor, $1 + 2.86[SO_2]/[CO]$, should be equal to a constant, $k_{1c}/(k_{1b} + k_{1c} + k_{2b})$. The values so determined are summarized in the last column of Table VII. Note that the data are constant within the experimental error over the entire wide range of reactant concentra-

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(16) The error limits shown here as elsewhere in the paper represent the 95% confidence limits (2σ) derived by the usual statistical methods assuming only random errors. Of course the absolute error in the values of the product and sensitized emission quantum yield data may be somewhat greater than these limits imply.

(17) K. Otsuka and J. G. Calvert, *J. Amer. Chem. Soc.*, **93**, 2581 (1971).

(18) Recent unpublished measurements of the rate constant for $^1SO_2$ quenching by benzene show that it is about twice that for SO_2: data of Dr. H. W. Sidebottom, to be published.

Table VII. Estimates of the Rate Ratio, $k_{1c}/(k_{1b} + k_{1c} + k_{2b})$, from the Benzene Inhibition of CO_2 Formation in the 3130-Å Photolysis of SO_2–CO Mixtures

Pressure reactants, Torr			
SO_2	CO	C_6H_6	$k_{1c}/(k_{1b} + k_{1c} + k_{2b}) \times 10^3$
2.21	375	7.00	2.4
4.64	111	1.46	2.2
4.64	111	2.00	1.8
4.64	111	2.42	1.6
4.64	111	2.42	1.9
4.64	111	2.42	2.0
4.64	111	2.58	1.6
4.64	111	∞[a]	1.6
4.64	375	7.00	2.2
11.0	375	3.00	2.9[b]
11.0	375	5.00	2.0
11.0	375	7.00	1.9
22.0	375	7.00	2.3
44.0	375	7.00	2.2
			Av[c] = $(2.0 \pm 0.6) \times 10^{-3}$

[a] Estimated from an extrapolation of the data of Figure 5. [b] This value was excluded in the average. [c] The error limits shown are twice the standard deviation (95% confidence limits).

tions employed. Thus the data are consistent with the participation of but one singlet state, the fluorescent state of SO_2. This result is at variance with the predictions based upon the results of Cehelnik, *et al.* They predict that the quantum yields of CO_2 from the nonoptical excited singlet state (SO_2^*) will be given by $\Phi_{CO_2}{}^* = P_{CO}/(4 \times 10^4 + 8.8 \times 10^3 P_{SO_2})$ with the pressures in Torr; their data suggest that the yield from the optical singlet state ($^1SO_2$) will be $\Phi_{CO_2}{}^S = 1.4 \times 10^{-3}/(1 + 2.80[SO_2]/[CO])$. By their mechanism choice the total quantum yield of CO_2 from the excited singlet states is very pressure dependent. Thus for our conditions of $P_{SO_2} = 2.21$ and $P_{CO} = 375$ Torr, $\Phi_{CO_2}{}^* + \Phi_{CO_2}{}^S = 7.7 \times 10^{-3}$ (error limits unknown), whereas we estimate $(2.0 \pm 0.6) \times 10^{-3}$; for our conditions of $P_{SO_2} = 4.64$, $P_{CO} = 111$ Torr, their equations predict the total singlet quantum yield of CO_2 to be 2.7×10^{-3} while we observe $(1.8 \pm 0.5) \times 10^{-3}$. The apparent difference observed between the singlet contribution estimated in this work and that found by Cehelnik, *et al.*, is not an artifact resulting from the different choices of triplet quenchers; they used biacetyl and nitric oxide while we chose benzene. The degree of quenching which they observed in their earlier work with added NO (Table III of ref 2) and biacetyl (Table II of ref 2) is entirely consistent with our benzene results. However, they found much less NO inhibition in a few later runs (Table VI of ref 2), and apparently based their conclusion concerning the part of the nonoptical triplet on these results. We believe these limited results to be in error.

A further set of experiments were carried out in an attempt to define further the nature of the singlet reactive state leading to CO_2. Nitrogen gas (20–291 Torr) was added to a mixture of CO (111 Torr), SO_2 (4.64 Torr), and benzene (2.58 Torr); see Table V. The object was to observe the quenching effect of nitrogen and check if this matched well that expected for the optical singlet state. However, any attempt at a quantitative treatment of the data is difficult and of questionable value. The difficulty lies in the estimation of the extent of enhancement of triplet generation on nitrogen addition. The increase results both from the larger intersystem crossing ratio for collisions with N_2 over those for CO and from a further larger effect at high pressures which we will consider later in the discussion. These increases tend to mask the occurrence of singlet quenching reactions with nitrogen. The parameters which control these effects are now sufficiently uncertain in magnitude to exclude confidence in their use to test the effect of N_2 addition quantitatively. However, it can be said that all of our present results are not inconsistent with the hypothesis of the excited fluorescent singlet of SO_2 as the origin of the CO_2 in the benzene quenched SO_2–CO mixture photolyses. Introduction of another nonemitting singlet species is entirely unnecessary to fit all of the evidence now at hand.

Nature of the Triplet Sulfur Dioxide Reactant in CO_2 Formation. Some additional key information related to the nature of the reactive triplet state or states leading to CO_2 formation can be had from a detailed consideration of the kinetics of the CO_2 inhibition by nitrogen and benzene. Assume for the moment that the contention of Cehelnik, *et al.*, is correct and that there are two triplet states, the phosphorescent state ($^3SO_2$) and some nonemitting triplet (SO_2^{**}), which react with CO to form CO_2. First, note the results of our 3530–3970-Å photolyses of SO_2–CO mixtures with added N_2 in section b of Table V. For the reactant concentrations employed and the known $^3SO_2$-quenching rate constants we would expect the fraction of $^3SO_2$ molecules quenched by nitrogen addition to be 0.32. This expectation compares well with the average fraction, 0.30, by which Φ_{CO_2} was suppressed by N_2 addition.[19] Obviously there is nothing peculiar about the $^3SO_2$ population and reactivity in this system, and we can conclude that the $^3SO_2$ state is not quenched to the SO_2^{**} state or any other reactive state by collisions with N_2. This is also in accord with the view of Cehelnik, *et al.*, who found it necessary to postulate the absence of interconvertibility of the $^3SO_2$ and SO_2^{**} states in order to explain the kinetics of CO_2 formation in the 3130-Å photolysis of SO_2–CO mixtures.

We would expect the mechanism of the generation of the triplets from singlets, whatever the kinetics might be in detail, to be unaffected by the addition of very small quantities of benzene since the vast majority of the deactivating collisions of excited singlets is with CO and SO_2 for our experiments. Then it is likely that the inhibition of CO_2 formation with added benzene results from reactions 14 and 15. The quenchable quantity of

$$^3SO_2 + C_6H_6 \longrightarrow (SO_2,\ C_6H_6,\ \text{or products}) \tag{14}$$

$$SO_2^{**} + C_6H_6 \longrightarrow (SO_2,\ C_6H_6,\ \text{or products}) \tag{15}$$

the CO_2 formed must be derived from reactions 9a and 16a; reactions 17 and 18 are alternative modes for SO_2^{**} removal based on an extension of the mechanism of Cehelnik, *et al.* If the rates of formation of $^3SO_2$

$$SO_2^{**} + CO \longrightarrow CO_2 + SO \tag{16a}$$

$$\longrightarrow CO + SO_2 \tag{16b}$$

$$SO_2^{**} + SO_2 \longrightarrow (2SO_2\ \text{or products}) \tag{17}$$

$$SO_2^{**} \longrightarrow SO_2 \tag{18}$$

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(19) Similar unpublished results were observed by Dr. Silvia E. Braslavsky with Professor Julian Heicklen of Pennsylvania State University; private communication to the authors.

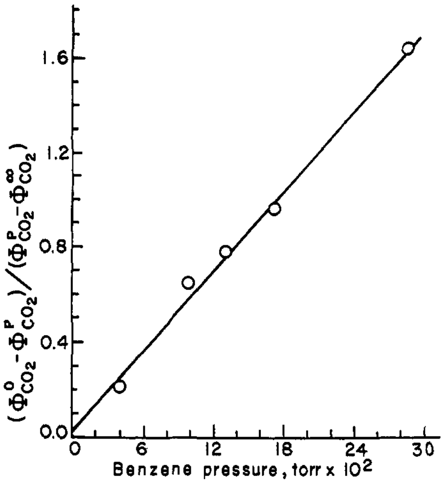

Figure 6. Plot of the function of the quantum yield of CO_2, relation H of the text, *vs.* the benzene pressure; data are from the benzene inhibited, 3130-Å photolyses of SO_2–CO mixtures of Table V; $P_{SO_2} = 4.64$, $P_{CO} = 111$ Torr; temperature, 30°.

and SO_2^{**} are R and R^{**}, respectively, then the mechanism I-18 leads to relation H

$$\frac{\Phi_{CO_2}{}^0 - \Phi_{CO_2}{}^P}{\Phi_{CO_2}{}^P - \Phi_{CO_2}{}^\infty} = \frac{[C_6H_6(\delta + \epsilon)]}{\zeta + \eta} \qquad (H)$$

where

$$\delta = \frac{Rk_{9a}k_{14}([CO]k_{16} + [SO_2]k_{17} + [C_6H_6]k_{15} + k_{18})}{[CO]k_9 + [SO_2]k_8}$$

$$\epsilon = \frac{R^{**}k_{16a}k_{15}([CO]k_9 + [SO_2]k_8 + [C_6H_6]k_{14})}{[CO]k_{16} + [SO_2]k_{17} + k_{18}}$$

$$\zeta = Rk_{9a}([CO]k_{16} + [SO_2]k_{17} + [C_6H_6]k_{15} + k_{18})$$

$$\eta = R^{**}k_{16a}([CO]k_9 + [SO_2]k_8 + [C_6H_6]k_{14})$$

Here $\Phi_{CO_2}{}^0$, $\Phi_{CO_2}{}^P$, and $\Phi_{CO_2}{}^\infty$ refer to the measured quantum yields of CO_2 formed in the SO_2–CO–C_6H_6 mixtures with $P_{CO} = 111$, $P_{SO_2} = 4.64$ Torr, and with benzene at 0, p Torr, and at a pressure which gives near complete triplet quenching, respectively. For the reactant concentrations employed in the experiments from which the data shown in Figure 5 were obtained, from relations F and G we can estimate the value of $\Phi_{CO_2}{}^T = 1.8 \times 10^{-3}$ and $\Phi_{CO_2}{}^S = 1.7 \times 10^{-3}$. Therefore one expects Φ_{CO_2} from SO_2^{**} to be about 2.7×10^{-3} for these conditions. In other words with the assumptions made we must have about 40 and 60%, respectively, of the CO_2 quenchable product derived from the $^3SO_2$ and the SO_2^{**} states. However, this conclusion based on the assumption of two reactive triplet states is not supported by the kinetic treatment of the data in Figure 6. Within the experimental error, the quantum yield function H shows a simple linear dependence with no obvious break in the slope of the line within the 40–60% triplet suppression points or elsewhere over the entire reliable range of the measurements. This result can only be expected if one of the following conditions are met: (1) by some fortuitous coincidence the same fraction of the $^3SO_2$ and SO_2^{**} species is quenched by benzene for any given benzene pressure employed; (2) there is only one reactive triplet state formed in this system. The first alternative is a physically improbable situation which requires the fortuitous match of a series of rate constant, reactant concentration terms in relation H, and it seems to be an untenable postulate. Since the quantitative rate data show the $^3SO_2$ state to be involved at least to the extent of about 40% of the CO_2 formed from triplets for our conditions, the second, most probable alternative demands that the only triplet reactant is $^3SO_2$. However, if this hypothesis is to be considered seriously, some additional source of $^3SO_2$ must come into being in runs at high pressures. If the single reactive triplet is the $^3SO_2$ state then relation H reduces to J. This form is consistent with experiment

$$\frac{\Phi_{CO_2}{}^0 - \Phi_{CO_2}{}^P}{\Phi_{CO_2}{}^P - \Phi_{CO_2}{}^\infty} = \frac{[C_6H_6]k_{14}}{[CO]k_9 + [SO_2]k_8} \qquad (J)$$

(Figure 6); from the slope of the plot (5.68 ± 0.54) together with the rate constants from lifetime studies for $^3SO_2$ quenching by CO [$k_9 = (0.87 \pm 0.06) \times 10^8$] and SO_2 [$k_8 = (4.2 \pm 0.1) \times 10^8$ l./(mol sec)] at 30°, we estimate the $^3SO_2$-quenching rate constant for benzene, $k_{14} = (6.3 \pm 0.9) \times 10^{10}$ l./(mol sec). In view of the error limits, this is a reasonable check on the value of k_{14} determined directly in previous $^3SO_2$ lifetime studies, $k_{14} = (8.1 \pm 0.7) \times 10^{10}$ l./(mol sec).[13] It is instructive to apply a similar treatment to the Φ_{CO_2} quenching data obtained by Cehelnik, *et al.*, in runs with $P_{CO} = 390$, $P_{SO_2} = 75$ Torr with added small quantities of nitric oxide (Table III of ref 2). Using the same mechanism assumptions, we estimate the $^3SO_2$-quenching rate constant for nitric oxide to be $(10.7 \pm 3.0) \times 10^{10}$ l./(mol sec). This is in accord with the value of this constant, $(7.4 \pm 0.3) \times 10^{10}$ l./(mol sec), from our direct measurements.[5] The limited data for biacetyl quenching of CO_2 formation reported by Cehelnik, *et al.* (their Table II), is also qualitatively consistent with the quenching expected for the $^3SO_2$ species although the data are insufficient to make a firm test of this. Thus it seems to be a reasonable hypothesis that only one triplet state of SO_2 is involved in CO_2 formation in SO_2–CO mixture photolyses within the first absorption band and that this is the phosphorescent state, $^3SO_2$. As we have seen, if this hypothesis is correct then some alternative source of $^3SO_2$ must become important at high pressures of reactants.

A Test of the Hypothesis of "Excess" Triplet Formation at High Pressures. A check was made on the hypothesis that an additional source of $^3SO_2$ appears as the pressure of the gas mixture is raised. The triplet-sensitized emission from biacetyl was observed in a series of runs at fixed $[SO_2] = 7.93 \times 10^{-4}$ M and $[Ac_2] = 3.17 \times 10^{-6}$ M, and with varied concentrations of added nitrogen gas ($0.85 \times 10^{-3} - 35.2 \times 10^{-3}$ M). The results are shown in Table II. It is instructive to compare these results with the expectations based on the simple low-pressure mechanism I-13. Reactions 1d, 2d, and 9c must be considered also in this

$$^1SO_2 + N_2 \longrightarrow SO_2 + N_2 \qquad (1d)$$

$$\longrightarrow {}^3SO_2 + N_2 \qquad (2d)$$

$$^3SO_2 + N_2 \longrightarrow N_2 + SO_2 \qquad (9c)$$

case. Using this mechanism relation K is anticipated.

$$(\Phi_{sens}/\Phi_{sens}{}^0)\theta\kappa = k_{2d}[N_2]/k_{2a}[SO_2] \qquad (K)$$

$\Phi_{sens}{}^0$ is the quantum yield of the sensitized phosphorescence emission of biacetyl in the binary mixture of SO_2

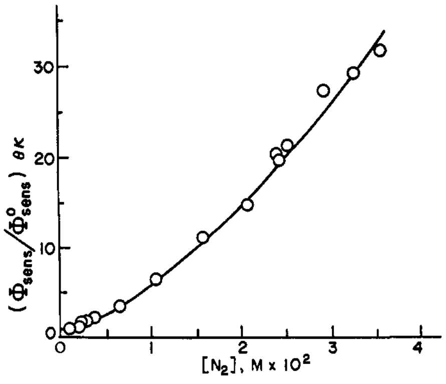

Figure 7. Plot of a function of the quantum yields of SO_2-triplet-sensitized phosphorescence in biacetyl (relation K of the text) *vs.* the nitrogen concentration; data are from the 2875-Å irradiated mixtures of SO_2 (7.93×10^{-4} *M*) and biacetyl (3.17×10^{-6} *M*) with added nitrogen gas.

(7.93×10^{-4} *M*) and biacetyl (3.17×10^{-6} *M*), while Φ_{sens} is that quantum yield for the ternary mixture of SO_2–biacetyl–N_2 with the same SO_2 and biacetyl concentrations as before but with added nitrogen gas: $\theta = 1 + \{(k_{1d} + k_{2d})/(k_{1a} + k_{2a})\}([N_2]/[SO_2])$ and $\kappa = 1 + \{k_{9c}[N_2]/(k_{10}[Ac_2] + k_8[SO_2])\}$. Taking $(k_{1d} + k_{2d})/(k_{1a} + k_{2a}) = 0.31$,[9] $k_{2d}/k_{2a} = 0.10$,[9] $k_{9c} = 8.5 \times 10^7$,[5] and $k_8 = 3.9 \times 10^8$ l./(mol sec),[15] values for θ and ϵ given in Table II were estimated for the reactant concentrations employed. A plot of the function K is shown in Figure 7. Since $[SO_2]$ was held constant in these runs, according to (K), we expect a linear relation between the variables. This is definitely not the result observed. The value of k_{2d}/k_{2a} defined by the slope at low pressures is consistent with the value reported previously (0.10 ± 0.03)[9] after the α correction for the pressure effect is made. However, it is evident that there is a strong deviation from the linear form predicted by relation K, and the simple low-pressure mechanism for $^3SO_2$ formation is not adequate to account for the triplet levels attained at high pressure. It clearly indicates that an entirely new source of triplet SO_2 molecules, presumably the $^3SO_2$ species, appears at high gas pressures.[20] Obviously the small suppression of the Φ_{CO_2} values observed with added nitrogen by Cehelnik, *et al.*, provides no evidence concerning the nature of the states involved. Both the increased intersystem crossing ratio with nitrogen added to the CO–SO_2 mixtures and the "excess" triplet generation at high nitrogen pressures would obscure the true quenching effect of added nitrogen in their experiments.

We suggest that a possible source of "excess" $^3SO_2$ lies in the additional $^1SO_2$ deactivation paths 1e–1g which parallel 1a, 1b, and 1c.

$$^1SO_2 + SO_2 \longrightarrow X + SO_2 \tag{1e}$$

$$^1SO_2 + CO \longrightarrow X + CO \tag{1f}$$

$$^1SO_2 + N_2 \longrightarrow X + N_2 \tag{1g}$$

$$X + SO_2 \longrightarrow (2SO_2) \tag{19a}$$

$$\longrightarrow {}^3SO_2 + SO_2 \tag{19b}$$

$$X + CO \longrightarrow SO_2 + CO \tag{20a}$$

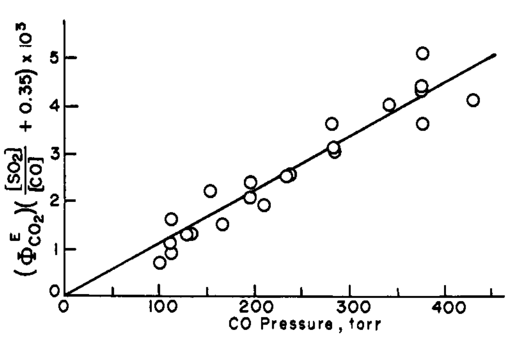

Figure 8. Plot of the simplified function of the "excess" carbon dioxide quantum yield (relation M of the text) *vs.* the CO pressure; values are calculated from the data of Table IV for all experiments with $[SO_2]/[CO] < 0.1$.

$$X + CO \longrightarrow {}^3SO_2 + CO \tag{20b}$$

$$X + N_2 \longrightarrow SO_2 + N_2 \tag{21a}$$

$$\longrightarrow {}^3SO_2 + N_2 \tag{21b}$$

$$X \longrightarrow SO_2 \text{ or other nonemitting products} \tag{22}$$

The nature of X remains uncertain. Presumably it could be an excited nonemitting singlet or triplet state of SO_2 or one of its unstable isomers S–O–O or cyclo-SO_2; however, it must not react with CO to generate CO_2 for the reasons outlined previously in ruling out two triplet reactants. The potential energy of X must be sufficiently high (about 75 kcal/mol above ground state SO_2) so that the generation of $^3SO_2$ in reactions 19b, 20b, and 21b is not energy deficient. In order for the kinetics of the triplet "excess" to reflect a first-order dependence on [CO], the effect both we and Cehelnik, *et al.*, observe (see the following discussion), the major reaction of X must be its unimolecular, nonradiative decay in (22). Hellner has recently observed a very long-lived, nonemitting transient in SO_2 flash photolysis which could conceivably be the X species of the mechanism outlined here.[21]

The reaction sequence outlined, 1e–1g, I-22, predicts that the triplet "excess" quantum yield of CO_2, defined as $\Phi_{CO_2}^{E} = \Phi_{CO_3}^{expt} - (\Phi_{CO}^{S} + \Phi_{CO_2}^{T})$, should be given by relation L. Obviously any such complex

$$\Phi_{CO_2}^{E} = \frac{\{([SO_2]k_{19b}/[CO]k_{20b}) + 1\}\{([SO_2]k_{1e}/[CO]k_{1f}) + 1\} \times (k_{9a}k_{20b}k_{1f})/k_9k_{20}(k_{1b} + k_{1c} + k_{2b} + k_{1f})}{\{([SO_2]k_8/[CO]k_9) + 1\}\{([SO_2]k_{19}/[CO]k_{20}) + 1 + (k_{22}/[CO]k_{20})\}\{([SO_2](k_{1a} + k_{2a} + k_{1e})/[CO] \times (k_{1b} + k_{1c} + k_{2b} + k_{1f})] + 1\}} \tag{L}$$

kinetic expression cannot be tested adequately with the very limited data now available. It can be seen, however, that the form is suitable to describe the data satisfactorily. For the condition of low $[SO_2]/[CO]$, it may be possible to make the following approximations; $([SO_2]k_{19b}/[CO]k_{20b}) + 1 \cong ([SO_2]k_8/[CO]k_9) + 1$, $[SO_2]k_{1e}/[CO]k_{1f} \ll 1$, $([SO_2]k_{19}/[CO]k_{20}) + 1 \ll k_{22}/k_{20} \cdot [CO]$, then the relation L reduces to M. In experiments

$$(\Phi_{CO_2}^{E})\left(\frac{[SO_2]}{[CO]} + 0.35\right) = \frac{k_{20b}k_{1f}k_{9a}[CO]}{k_9k_{22}(k_{1a} + k_{2a} + k_{2e})} \tag{M}$$

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[20] Dr. Angelo Fatta and Professor Julian Heicklen have told us of similar observations with excess of added biacetyl to SO_2. However, for their conditions biacetyl molecules quench the $^1SO_2$ species significantly so that the results are less readily interpreted than our own.

[21] C. Hellner, Department of Chemistry, National Bureau of Standards, Washington, D. C., personal communication to the authors.

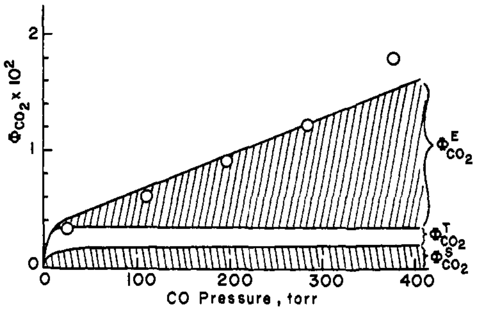

Figure 9. Plot of the theoretical curves for the quantum yields of CO_2 from excited $^1SO_2$ ($\Phi_{CO_2}{}^S$ of relation G), $^3SO_2$ from the low-pressure mechansim ($\Phi_{CO_2}{}^T$ of relation F), and the "excess" triplet ($\Phi_{CO_2}{}^E$ of relation M) *vs.* the pressure of carbon monoxide; calculated for the 3130-Å photolyses of SO_2–CO mixtures at P_{SO_2} = 2.0 Torr; the open circles represent the experimentally measured quantum yields of carbon dioxide.

at sufficiently low $[SO_2]/[CO]$ ratio we expect the function $(\Phi_{CO_2}{}^E)\{([SO_2]/[CO]) + 0.35\}$ to be a linear function of [CO]. A test of this dependence is shown in Figure 8 using all data for runs in Table IV for $[SO_2]/[CO] < 0.1$. The expected linear form is at least qualitatively consistent with these data. The slope of the line, 1.12×10^{-5} Torr^{-1}, may be taken as equal to the constant terms on the right side of relation M and equation N may be used to calculate the approximate

$$\Phi_{CO_2}{}^E = 1.12 \times 10^{-5} P_{CO}\ (\text{Torr})/(0.35 + [SO_2]/[CO]) \quad (N$$

values of $\Phi_{CO_2}{}^E$. It is instructive to test the compatibility of all the Φ_{CO_2} data with the values of the total quantum yields calculated from relations F, G, and N. This has been done for runs at P_{SO_2} = 2.0 Torr and varied P_{CO}, and the data are plotted in Figure 9. The experimentally measured values of Φ_{CO_2} appear as circles on the plot. It is seen that the theoretical functions F and G account for most of the CO_2 in runs below CO pressures of about 5 Torr, but the dominant source at high CO pressures is the $^3SO_2$ formed in the high-pressure mechanism. The total quantum yields of CO_2 calculated for each of the runs are shown in Table IV. In general the data are reproduced quite well for all the runs. The largest deviations occur at the high $[SO_2]/[CO]$ ratios where the function M does not reduce accurately to the approximate function N. Obviously a more judicious choice (within the error limits of the experimental rate constant estimates) could be made in the values used for the rate constants in the theoretical functions F and G, and a more complete form of the function N could be employed to fit the experimental data more precisely. There is no point in this exercise at this stage of our knowledge in these systems.

The present work confirms the interesting observations of Cehelnik, *et al.*, that the simple low-pressure mechanism of $^3SO_2$ formation cannot alone account for CO_2 formation in 2400–3200-Å irradiated mixtures of SO_2 and CO at high pressures of the reactants. However, all of our results favor the conclusion that the only reactive SO_2 states in these systems are the fluorescent singlet and the phosphorescent triplet. The significant participation of two new nonemitting singlet and triplet states of SO_2 in CO_2 formation seems unlikely to us. Our results favor the involvement of some undefined intermediate excited state or unstable isomer of SO_2 (X), not as a reactant with CO to form CO_2 directly, but as a new source of phosphorescent triplet in experiments at high reactant pressures. We are continuing tests of these systems to check the alternative hypotheses further.

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Kinetics of Proton-Transfer Reactions. V.
A Linear Free Energy, Enthalpy, and Entropy System

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Abstract: Rate and equilibrium data as a function of temperature are reported for the deprotonation of a series of seven closely related internally hydrogen-bonded weak acids by means of hydroxide ions. The compounds studied all had an ortho azo or salicylate internal hydrogen bond. Not only are the free energies of activation linearly related to the free energies of reaction (α_G = 1.1), but the enthalpies and entropies of activation are linearly related to the enthalpies and entropies of reaction, respectively (slopes 1.0 and 1.4). The consequences of these results are discussed in relation to the origin of the Brønsted relationship for these compounds.

In earlier papers,[1,2] we presented rate and equilibrium data for the reaction of a series of internally hydrogen-bonded acids with OH^-. A graph of log k_f, the forward (deprotonation) rate constant, *vs.* pK_a gen-

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(1) M. C. Rose and J. E. Stuehr, *J. Amer. Chem. Soc.*, **90**, 7205 (1968).

(2) M. C. Rose and J. E. Stuehr, *ibid.*, **93**, 4350 (1971).